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Synthesis and crystal structures of three new rhenium(I)-tricarbonyl diimine complexes

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Rhenium tricarbonyl diimine complexes have been the subject of much attention, mainly because of their photophysical and photochemical properties and their use in CO₂ activation and in supramolecular chemistry and catalyst [1]. Such Re(I) complexes are ideally suited for solar energy conversion dyes, since they display intense luminescence in the visible region of the spectrum with long emission lifetimes. The origin of the emission was attributed to the metal-to-ligand charge transfer (MLCT) state. The photochemical and photophysical properties of these complexes can be fine-tuned by changing the chromophoric, bidentate ligand and/or the ancillary "spectator" ligands [2]. The structures of the newly prepared N,N-bis-(diimine)-tricarbonyl rhenium(I) complexes, [Re(CO)₃(L)(X)] (X = Cl, CF₃COO and L = chelating diimine), determined by X-ray diffraction show that the complexes are the facial isomers and are of distorted octahedral geometries. To the best of our knowledge, there are only few reports concerning the structural analysis of these complexes in which the R is carboxylate group.

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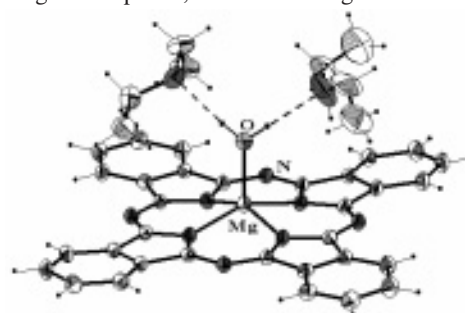
Aqua magnesium(II) phthalocyanine bis(diethyl-amine) solvate

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Magnesium phthalocyanine (MgPc) and its MgPcL and MgPcL₂ coordination complexes (4+1 and 4+2) with N and O donor ligands deserve attention first of all because of similarity with chlorophyll, thus being its synthetic models. Due to their electrochemical properties they find application in solar energy conversion, are used as pigments in optical disks, laser printers and display devices. Particular interest in aquamagnesium phthalocyanine (also known as 'X-phase') is concerned with its solid-state intense near-IR absorption band, which origin is not completely clear up to now. Two of the works dedicated to the problem give completely different explanation: first assigns MgPc(H₂O)₂ composition to the 'X-phase' and suggests that the near-IR absorption arises from extinction coupling effects [1], second analyses crystal structures of triclinic and monoclinic modifications of MgPc(H₂O), of which only triclinic one exhibits near-IR absorption. Similarity of the structures of triclinic MgPc(H₂O) and β-MgPc, which also exhibits the phenomenon of near-IR absorption, suggests that the origin could be found in formation of face-to-face Π-Π stacked dimers [2]. Violet crystals of the title compound were obtained by recrystallization of MgPc from diethylamine solution, sealed under vacuum in glass ampoule, at 50 °C during 12 hours.



Structure of MgPc(H₂O)•2Et₂NH is built of MgPc(H₂O) moieties, stacked in dimers by back-to-back fashion. These dimers pack together *via* very weak hydrogen-bond interactions of C-H...N type into infinite planes perpendicular to c-axis direction at 0 and ½ height of the unit cell. Two diethylamine moieties are in the outer coordination sphere, attached to water molecule by O-H...N hydrogen bonds (1.94(2), 1.97(2) Å and 172(2), 167(2)° for H...N distances and O-H...N angles, respectively). N-H protons are not involved in any H-bond formation. The ethyl groups exhibit high thermal librations. Mg atom deviates from N₄-isoindole plane by 0.494(2) Å. This distance is somewhat longer (by -0.04 Å) than the ones in two polymorphs of MgPc(H₂O). The Mg-O(H₂) distance (1.993(2) Å) and four Mg-N_{isoindole} distances (2.038(2)-2.040(2) Å) are comparable with the appropriate values in the MgPc(H₂O). Saucer-shaped geometry would be an expected one for 4+1 coordinated MgPc moiety, but it is considerably distorted by flattering through repulsive π-π interactions between two Pc rings, which are overlapped along isoindole-nitrogen axis.

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